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RESISTANCE OF THIN FILMS TO ACID SOLUTIONS

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The dynamics of interaction between thin sol-gel films and acid solutions is described. It is established that two opposite processes occur simultaneously. Whereas swelling increases, dissolution decreases the coating thickness. The effect of acid concentration and pickling duration on these phenomena is described. The change of the refractive index of films after their reaction with the aggressive medium is estimated and explained.

One of the main service characteristic of glass materials used for light-transparent openings is their capacity of preserving such physical properties as luster, color, and clarity for a long time. Moisture, acid vapors and active gases that are present in air impair to a certain extent the above characteristics. Lately glazing is frequently done with sheet glass modified by multifunctional clear films. To predict the durability of such materials, one needs data on the destruction of coatings in chemically active media. The purpose of the present work is to study the kinetics of the dissolution of thin-layer sol-gel films in acids.

The studies were performed on large-size glass (1100 × 2000 × 4 mm) with a highly reflective multicomponent sol-gel film deposited on its surface (USSR Inventor's Certif. No. 1799856). The coating was fixed by firing at 450°C for 30 min. Samples of size 50 × 50 × 4 mm were cut out from this glass and exposed at room temperature in aqueous solutions of hydrochloric and nitric acids. The refractive index and the film thickness before pickling n and h, after pickling n_1 and h_1, and after pickling and subsequent firing for 30 min at 450°C n_2 and h_2 were measured using a LÉF 3M1 ellipsometer.

Figure 1 shows a microphoto of the film considered obtained with an UÉMV-100K electron microscope. Extended chain elements up to 0.05 μm thick that are clearly visible are identical to the structures formed in high-molecular compounds [1]. This gives reason to analyze processes occurring in film pickling in the context of notions used for interaction of a high-molecular compound with a solvent.

The experimental results indicate that the film thickness h_1 after exposure in an acid solution (pickling) in some cases is larger than the initial thickness h. This phenomenon in the chemistry of high-molecular compounds is called "swelling" and is estimated by the degree of swelling and expressed as follows:

$$\alpha = \frac{m - m_0}{m_0},$$

where m_0 and m are the weights of the initial and the swollen polymer, respectively.

Swelling can be limited, when α reaches a limiting constant value, or unlimited, when α passes through a maximum, after which the polymer becomes dissolved. In this case swelling constitutes the initial stage of dissolution [1]. To estimate the degree of swelling of thin films, we accepted the above formula with minor modifications:

$$\alpha_{pic} = \frac{h_1 - h}{h} \times 100,$$

where h and h_1 are the film thickness before and after pickling, respectively.

To estimate the true modification of thickness, the treated film was fired at a temperature of 450°C for 30 min to remove the residual solvent. The chemical resistance was estimated using the expression

$$T = \frac{h - h_2}{h} \times 100,$$

where h and h_2 are the thickness of the initial film and the film after pickling and subsequent firing, respectively.

Table 1 gives the pickling conditions and the variation of film thickness after exposure to hydrochloric acid solutions α_{pic} and after exposure with subsequent firing T.

Figure 2 shows the variation of the degree of swelling of films depending on the concentration of acid and treatment duration. After 1 min treatment the value α_{pic} consistently grows, reaching its maximum in 0.10 N solution and then in-

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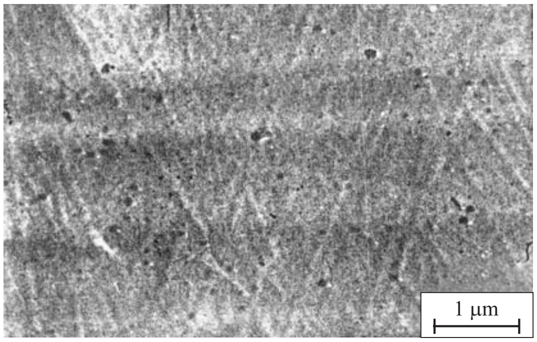

Fig. 1. Microphoto of film coating (× 10,000).

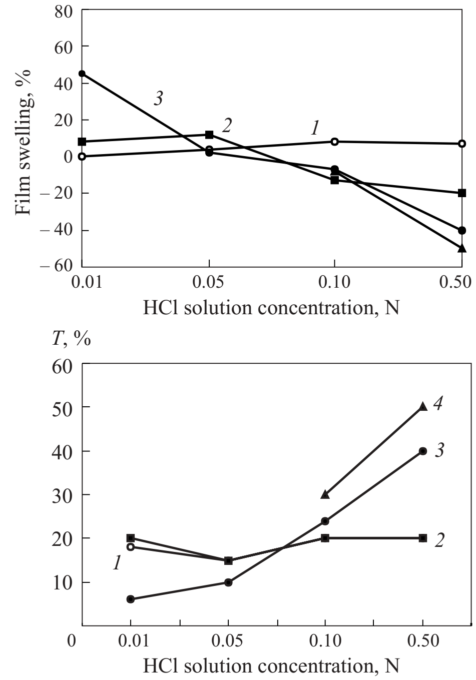

Fig. 2. The dependence of the degree of swelling of films and the value T on the concentration of hydrochloric acid solution and pickling duration: *1*, *2*, *3*, and *4*) treatment duration of 1, 30, 60, and 120 min, respectively.

significantly decreases. If the treatment duration is 30 min, obvious swelling is registered only in 0.01 and 0.05 N solutions. A further increase in hydrochloric acid concentration intensifies the dissolution of the film, which is manifested in the final decrease of its thickness, with the value α_{pic} becoming negative. After the pickling of the coating for 60 min a similar phenomenon is observed, but in the latter case dissolution starts already in 0.05 N acid.

Consequently, the reaction between the film and the acid is made up of two contradictory processes: swelling and dissolution. The former increases and the latter decreases the film thickness. The increase in growth is observed under a low concentration of acid or a short duration of treatment. An increase in concentration perceptibly intensifies dissolution; therefore, the swelling effect is concealed and the film thickness with respect to its initial value decreases.

It follows from the data in Table 1 that the value of α_{pic} in 0.01 N acid grows from 0 to 45% in proportion to treatment duration. After pickling for 30 min in 0.05 N and 1 min in 0.10 and 0.50 N solutions the swelling efface is still perceptible; a further increase in exposure duration facilitates the dissolution of the coating and decreases α_{pic} to negative values, i.e., the swelling of films after 1 min of exposure, same as dissolution after 60 and 120 min treatment, is proportional to acid concentration.

Thus, an increasing concentration stimulates two opposite phenomena: swelling under an insignificant pickling duration and dissolution after the treatment duration grows to 60 and 120 min. Table 2 shows the thickness and the refractive index of the coating before and after exposure in nitric acid solutions and specifies the pickling conditions.

It can be seen that the swelling effect is registered in the film treated for 1 min in 0.10 N nitric acid, whereas the value α_{pic} is 2.5 times higher than pickled in hydrochloric acid of the same concentration. In other cases the dissolution rate is so high that α_{pic} takes a negative value. The destructive effect of nitric acid is more evident than that of hydrochloric acid; therefore, the absolute values of α_{pic} are always greater. Therefore, after an exposure in an aggressive medium the film thickness is determined by two opposite processes: swelling and dissolution.

Figure 2 gives the dependence of the value T on the concentration of hydrochloric acid solution and pickling duration. Regardless of solution concentrations, the destruction of films after 1 and 30 min exposure virtually does not change and fluctuates within the limits of 15 – 20%. As the

TABLE 1

Solution concentration, N	Pickling duration, min	Film thickness variation, %		Distribution interval of refractive index values in films		
		α_{pic}	T	initial	after pickling	after pickling and subsequent firing
0.01	1	0	18	2.02 – 1.93	2.09 – 2.00	2.07 – 2.01
0.05	1	4	15	2.04 – 1.91	2.05 – 2.02	2.09 – 2.06
0.10	1	8	20	1.97 – 1.93	2.06 – 1.95	2.17 – 2.09
0.50	1	7	20	2.08 – 1.97	2.10 – 2.02	2.17 – 2.08
0.01	30	8	20	2.07 – 1.95	2.12 – 1.99	2.16 – 2.07
0.05	30	12	15	1.97 – 1.94	2.04 – 1.93	2.13 – 1.98
0.10	30	– 13	20	1.96 – 1.93	2.07 – 2.03	2.10 – 2.06
0.50	30	– 20	20	2.11 – 2.00	2.06 – 1.91	2.06 – 1.95
0.01	60	45	6	2.03 – 1.95	1.99 – 1.89	2.07 – 1.97
0.05	60	2	10	1.96 – 1.94	2.06 – 1.97	2.03 – 1.94
0.10	60	– 7	24	2.02 – 1.93	2.00 – 1.95	2.06 – 1.96
0.50	60	– 40	40	2.06 – 1.97	1.94 – 1.89	1.89 – 1.89
0.10	120	– 8	30	2.06 – 1.95	2.02 – 1.93	2.07 – 2.01
0.50	120	– 50	50	2.02 – 1.92	1.71 – 1.70	1.67 – 1.65
0.10	180	– 4	23	1.97 – 1.95	1.98 – 1.96	2.02 – 2.00

TABLE 2

Solution concentration, N	Pickling duration, min	Film thickness variation, %		Distribution interval of refractive index values in films		
		α_{pic}	T	initial	after pickling	after pickling and subsequent firing
0.10	1	20	6	2.10 – 2.07	2.02 – 2.01	2.12 – 2.08
0.05	30	– 30	18	2.05 – 2.04	2.15 – 2.05	2.11 – 2.08
0.10	30	– 15	20	2.04 – 1.98	2.08 – 1.92	2.10 – 2.02
0.50	30	– 40	60	2.12 – 2.08	2.09 – 1.99	2.13 – 2.10
0.01	60	– 16	20	2.13 – 2.08	2.07 – 2.00	2.16 – 2.12
0.10	60	– 12	22	2.12 – 2.03	2.08 – 2.06	2.14 – 2.13
0.10	120	– 15	30	2.06 – 2.00	2.11 – 1.97	2.14 – 2.13
0.10	180	– 25	26	2.06 – 2.03	2.06 – 2.01	2.08 – 2.00

treatment duration grows to 60 and 120 min, the value T increases in proportion to the concentration. When pickling is carried out in 0.01 and 0.05 N acids, increasing the treatment duration to over 30 min inhibits the destruction of films. Within the experimental error limits the value T for a coating exposed in nitric acid (Table 2) is virtually the same as in hydrochloric acid solutions of the same concentration.

Based on the above data it can be inferred that the true destruction of coatings (i.e., their chemical resistance) is little sensitive to the type of acid and has a rather complex dependence on acid concentration and treatment duration. Under 1 – 30 min treatment the value T is virtually constant. After a further exposure in low-concentration solutions the process may be delayed. If the HCl content is at least 0.10 N, the value T increases proportionally to the concentration and pickling duration.

Variations in optical properties, in particular the refractive index of the coating after its contact with the aggressive medium, are of interest. The analysis of the results in Tables 1 and 2 shows that in the overwhelming majority (70%) of cases the refractive index after pickling does not change; yet an insignificant growth is registered in 13% of the films and a decrease in 17% of the films. After pickling and subsequent firing the refractive index in most cases does not change (39%) or grows (52%) and only in 9% of cases does it decrease. The decrease in the refractive index occurs after pickling in 0.50 N hydrochloric acid for 60 or 120 min. The films in this case are significantly destroyed: T reaches maximum values of 40 and 50%.

Let us consider the possible reasons for the variations of the refractive index of the coating.

It is known that a thin film is an amorphous highly porous solid body [2], and its refractive index according to the data in [3] is found from the expression

$$n_{\text{ef}} = n_1 - \text{Por}\,(n_1 - n_3) - (n_2 - n_3)\, f(P/P_0),$$

where n_1, n_2, and n_3 are the refractive indexes of the skeleton material, adsorbed water, and air, respectively; $f(P/P_0)$ is the adsorption isotherm equation in its general form; Por is porosity.

As the aqueous solution reacts with the air-dry porous material, its pores become filled with water and the dissolving material, whose refractive indexes are significantly higher than that of air, which regularly increases the refractive index. Exposure of films in solutions is accompanied by their swelling, due to which the pores become partially or fully eliminated, and consequently the refractive index of the coating grows. It is known [4] that the sol-gel film considered in the present study becomes enriched with sodium and calcium oxides migrating from the glass substrate in an amount of 18.1 and 4.4 mol.%, respectively. After subsequent pickling in an acid solution, mobile calcium and sodium can partly become leached, causing a regular growth of the refractive index.

The secondary ion mass-spectroscopy method was used to identify the distribution of titanium and sodium in the coating considered. It is established that the greater the decrease in film thickness after pickling, the higher its concentration of low-refraction sodium and the greater its depletion of high-refraction titanium; consequently, the refractive index of such coating should be lower. The results of experiments in 0.50 N hydrochloric acid corroborate this assumption.

Thus, the reaction of film with acid is made up of two opposite processes: swelling and dissolution. An increasing acid concentration leads to swelling under a short pickling duration and to dissolution after the treatment duration increases to 60 and 120 min.

The change in the thickness of pickled films after their additional firing is little sensitive to the type of the acid and depends on acid concentration and treatment duration. With 1 – 30 min treatment the value of T is virtually constant. With a longer treatment in low-concentration solution, the process becomes inhibited. If the HCl content is at least 0.10 N, the value of T grows in proportion to the concentration and to the pickling duration.

In the majority of cases the refractive index of the films does not change after pickling. After pickling and subsequent firing, the refractive index either remains unchanged or grows. After protracted treatment in a concentrated acid solution accompanied by a significant decrease in the film thickness the refractive index may decrease.

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